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INVESTIGATION OF PHOSPHORUS-CONTAINING COMPOUNDS BASED ON
DIALKYL HYDROQUINONE DERIVATIVES AS ADDITIVES FOR LUBRICATING OILS

by

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INVESTIGATION OF PHOSPHORUS-CONTAINING COMPOUNDS BASED ON DIALKYL HYDROQUINONE DERIVATIVES AS ADDITIVES FOR LUBRICATING OILS

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(U) Some phosphites prep'd. from 2,5-di-tert-butylhydroquinone (I) and 2,5-di-tert-amylohydroquinone (II) contg. 6.2-8.9 percent P, were investigated as additives for diesel oil fuel. The stability of the oil with 0.1 percent of these additives, detd. as time necessary for absorbing 10 ml. 0 at 175 degrees, increased from 255 to 340-388 min. The corrosiveness of the oil with 1 percent additives decreased from 360 to 57-0.9 g./ml. (super-script 2) in the presence of 0.02 percent Cu naphthenate at 150 degrees for 25 hrs. Also, the film-formation coeff. decreased simultaneously. The most efficient were the additives prep'd. by condensation of phenyl-, and p-tert-amylophenylphosphorous acids with I and II, regarding both stability and anticorrosive properties. The formulas of the additives and their effects on the corrosiveness and stability of the oil are tabulated.

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The evaluation of the action of these compounds on the performance qualities of Diesel oil D-11 was done by existing methods. The stability of oil D-11 with 1% of the indicated compounds was determined by the method of the V. V. Kuybyshev Azerbaijhan Scientific Research Petroleum Institute (AZNII) at the temperature of 175°, and the anti-corrosion properties by the method of the Central Scientific Research Institute of Automobile and Automobile engines (NAMI) in the presence of 0.02% copper naphthenate over 25 h at 140°, while for thermal stability the Papok method was used at 250°.

INVESTIGATION OF PHOSPHORUS-CONTAINING COMPOUNDS BASED ON DIALKYL HYDROQUINONE DERIVATIVES AS ADDITIVES FOR LUBRICATING OILS

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To improve the stability and other performance qualities, lubricating oils are treated with a number of additives which contain nitrogen, phosphorus, a hydroxyl group, and other functional groups and elements.

The majority of these additives are obtained from alkylphenols, alkylthiophenols, derivatives of naphthalene hydrocarbons and other classes of organic compounds [1-3]. For the purpose of obtaining new types of additives we performed the synthesis of phosphites, using dialkyl derivatives of hydroquinone using as the original material.

The phosphites were obtained by the condensation reaction of 2,5-di-*tert*-butyl-4-oxyphenyl-dichlorophosphite with heptyl, octyl, nonyl, and decyl alcohols [4]. Spectroscopic investigation of the structure of the synthesized compounds enabled us to introduce some correctives into the formulas which we presented earlier for these compounds. As a result of further investigations in this direction the synthesis of a number of phosphites containing from 0.2 to 8.2% phosphorus was accomplished. Analysis showed that the values for the elemental composition of the synthesized compounds were close to the corresponding theoretically computed values. Later studies were carried out of the influence of the obtained compounds on the performance properties of lubricating oils.

The results of the tests of oil D-11 with various additives are given in Tables 1 and 2.

It was made clear that the investigated product have an effective action on the stability of oil D-11 in tests by the AZNII method, since the time of absorption of 10 ml of oxygen is increased from 255 to 340-363 min.

One should note that the productive interactions of phenol monochloroanhydrides and alkyl phenol with dialkyl hydroquinones have definite advantages as compared with phosphites in terms of effectiveness of the action on the stability of oil D-11. The former increase the time of absorption of 10 ml by 140 min and the latter by 90-100 min.

The data presented in Table 1 show that the synthesized compounds reduce considerably the corrosion of Diesel oil. With their addition in the amount of 1% the corrosion of the oil is reduced from 360 to 57-99 g/m². When added to Diesel oil in the amount of 0.5-1% the indicated compounds also bring about a considerable improvement in the thermal stability of the oil and reduce the factor of lacquer deposition. Good results were obtained with the addition to oil D-11 of the additives Nos. 6, 7, and 8, which are products of the condensation of monochloroanhydride of phenyl- and *n*-*tert*-amylphenyl phosphorous acid with 2,5-di-*tert*-butyl-hydroquinone. These condensation products proved to be most effective, both in relation to improvement in the stability of the oil and in relation to their anticorrosion properties.

Table 1. Study of the influence of synthesized compounds on the anticorrosion properties and thermal stability of oil D-11.

additive no.	Proposed formula of compound	Thermal oxidation stability factor, $\frac{t_{50}}{t_0}$			correlation coefficient per NBS method, R^2	
		lemon oil additive	stearic acid additive	largest residue, mg.		
1	oil without additive	—	—	0.98	22	260
2	oil + $(C_{14}H_{29}CH_2CO)P(OH)_2$	6.5	47	0.65	14	22.6
3	oil + $(C_{14}H_{29}CH_2CO)P(OH)_2$	1.9	53	0.17	9	23
4	oil + $(C_{14}H_{29}CH_2CO)P(OH)_2$	6.5	49	0.31	19	37
5	oil + $(C_{14}H_{29}CH_2CO)P(OH)_2$	1.9	55	0.16	6	43
6	oil + $(C_{14}H_{29}CH_2CO)P(OH)_2$	6.5	58	0.16	9	37
7	oil + $(C_{14}H_{29}CH_2CO)P(OH)_2$	1.9	49.5	0.10	9	26.5
8	oil + $(C_{14}H_{29}CH_2CO)P(OH)_2$	6.5	53	0.23	1	+2.4
9	oil + $(C_{14}H_{29}CH_2CO)P(OH)_2$	1.9	49.5	0.16	7.5	+4.3
10	oil + $(C_{14}H_{29}CH_2CO)P(OH)_2$	6.5	—	—	—	50.3
11	oil + $(C_{14}H_{29}CH_2CO)P(OH)_2$	1.9	51.5	0.18	13	10.7
12	oil + $(C_{14}H_{29}CH_2CO)P(OH)_2$	6.5	49.5	0.37	15	23
13	oil + $(C_{14}H_{29}CH_2CO)P(OH)_2$	1.9	—	—	—	43
14	oil + $(C_{14}H_{29}CH_2CO)P(OH)_2$	6.5	49.5	0.22	15	23
15	oil + $(C_{14}H_{29}CH_2CO)P(OH)_2$	1.9	53	0.14	43	+2.4

Conclusions

1. A number of new compounds containing phosphorus were synthesized in the basic of 2,5-di-tert-butylhydroquinone and 2,5-di-tert-amylhydroquinone.

2. It was established that the investigated compounds are effective additives which improve the stability and anti-corrosive properties of the oil D-11.

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Table 2. Study of influence of synthetic compounds on stability of oil D-11.

stability per 100 ml method, R_{100}	duration time of 10 ml evaporation period	stability per 100 ml method, R_{10}	
		oil without additive	oil + additive No. 1
51	215	—	—
61	342	—	—
63	352	—	—
64	355	—	—
65	346	—	—
66	367	—	—
67	354	—	—
68	363	—	—

Table 2. Study of influence of synthetic compounds on stability of oil D-11.